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1 **Structural controls on the location and distribution of CO₂ emission at a natural CO₂ spring in** 2 **Daylesford, Australia**

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8 **Abstract**

10 Secure storage of CO₂ is imperative for carbon capture and storage technology, and relies on a
11 thorough understanding of the mechanisms of CO₂ retention and leakage. Observations at CO₂
12 seeps around the world find that geological structures at a local and regional scale control the
13 location, distribution and style of CO₂ emission. Bedrock-hosted natural CO₂ seepage is found in the
14 Daylesford region in Victoria, Australia, where many natural springs contain high concentrations of
15 dissolved CO₂. Within a few meters of the natural Tipperary Mineral Spring, small CO₂ bubble
16 streams are emitted from bedrock into an ephemeral creek. We examine the relationship between
17 structures in the exposed adjacent outcropping rocks and characteristics of CO₂ gas leakage in the
18 stream, including CO₂ flux and the distribution of gas emissions. We find that degassing is clustered
19 within ~1 m of a shale-sandstone geological contact. CO₂ emission points are localised along bedding
20 and fracture planes, and concentrated where these features intersect. The bubble streams were
21 intermittent, which posed difficulties in quantifying total emitted CO₂. Counterintuitively, the
22 number of bubble streams and CO₂ flux was greatest from shale dominated rather than the
23 sandstone dominated features, which forms the regional aquifer. Shallow processes must be
24 increasing the shale permeability, thus influencing the CO₂ flow pathway and emission locations.
25 CO₂ seepage is not limited to the pool; leakage was detected in subaerial rock exposures, at the
26 intersection of bedding and orthogonal fractures.

27 These insights show the range of spatial scales of the geological features that control CO₂ flow.
28 Microscale features and near surface processes can have significant effect on the style and location
29 and rates of CO₂ leakage. The intermittency of the bubble streams highlights challenges around
30 characterising and monitoring CO₂ stores where seepage is spatially and temporally variable. CCS
31 monitoring programmes must therefore be informed by understanding of shallow crustal processes
32 and not simply the processes and pathways governing CO₂ fluid flow at depth. Understanding how
33 the CO₂ fluids leaked by deep pathways might be affected by shallow processes will inform the
34 design of appropriate monitoring tools and monitoring locations.

35 **Keywords:** CO₂ flux; CO₂ storage; mineral springs; CO₂ leakage; natural analogues

36

37 **Introduction**

38 Carbon Capture and Storage (CCS) is an important component of CO₂ emission reduction strategies
39 (OECD/IEA, 2015). Legislation and guidelines developed for CCS have set performance requirements
40 to minimise leakage risk (Dixon et al., 2015). For CCS to be an effective mitigation strategy the
41 injected CO₂ must remain securely in the subsurface (Schaffer et al., 2013). To avoid CO₂ leakage,
42 site selection criteria must be guided by a thorough understanding of the geological characteristics
43 that are most relevant to site integrity (Carpenter et al., 2011; Pearce and Czernichowski-Lauriol,
44 2004). As such there has been considerable research effort to understand the crustal fluid pathways
45 of CO₂ migrating from depth (Holloway et al. 2007; Oldenburg and Lewicki, 2006; Roberts et al.,
46 2017a). However there have been far fewer studies on fluid pathways in the near-surface. Effective
47 surface monitoring strategies to detect and quantify CO₂ leakage from geologic stores therefore
48 need to include an understanding of how near-surface processes affect leakage expression (Feitz et
49 al., 2014; Jenkins et al., 2015; Roberts et al., 2017b).

50 Studies of natural analogues identify that geological structures, such as faults, govern CO₂ fluid flow
51 on a macroscale (Dockrill and Shipton, 2010; Burnside et al., 2013; Miocic et al., 2016; Roberts et
52 al., 2017a). Fractures are also known to be an important control for fluid flow at meso- and micro-
53 scale e.g. (Bond et al., 2013; 2017; Roberts et al., 2014), and the presence of fractures have
54 complicated injection operations at pilot CCS sites (Rinaldi and Rutqvist, 2013; Verdon et al., 2013).
55 To date, there has been little focus on the influence of microscale features, such as bedding planes
56 and small fractures within foliated planes, on the surface expression of leaking CO₂—though these
57 features are known to affect geofluid flow (Faulkner et al., 2010; Hippler, 1993; McCay et al., 2018).

Further, field experiments designed to mimic CO₂ seepage by controlled CO₂ release at shallow depths have found CO₂ flow pathways are influenced by a number of local factors, and thus the location and style of seepage is difficult to predict (Roberts and Stalker, 2017). Thus, current understanding of the surface processes that govern CO₂ flow is limited. Here, we address this knowledge gap by presenting the characteristics of CO₂ leakage at Tipperary Mineral Spring, Daylesford (Victoria, Australia) where naturally occurring CO₂ seeps from exposed bedrock.

Geology and Hydrology of the Daylesford region

The Daylesford region in the Central Highlands of Victoria hosts over sixty mineral springs that are naturally rich in dissolved CO₂ (Cartwright et al., 2000; Laing, 1977; Shugg, 1996; Wishart and Wishart, 1990). These waters have historically been of economic importance to the region, facilitating commercial water bottling operations, health spas, and tourism (Lawrence, 1969). Although the mineral springs were first described by European settlers in the 1830s (Wishart and Wishart, 1990), mining activities in the Victorian Gold Rush (1850s - 60s) informed much of the current understanding of the geology and hydrology within the Daylesford area.

The regional geology comprises three principal units: deformed Ordovician turbidites of the Castlemaine Group, Devonian granites, and Quaternary basalts of the Newer Volcanics Province (VandenBerg, 1978) (Figure 1). The turbidites consist of greenschist facies slates, shales, and sandstones in a 4500 m thick flysch sequence. These were extensively folded, fractured, and faulted in a single deformation event, the Tabberabberan Orogeny, estimated to have caused a 50-70% crustal shortening of this province (Cox et al., 1991a; Gray and Willman, 1991; VandenBerg, 1978; Gray et al., 1991). The timing of the orogeny is constrained by the coeval intrusion of granitoids, which date to the Late Devonian (Richards and Singleton, 1981). The regional structure is now dominated by NNW trending folds that extend up to 100 km in length with wavelengths between 10-15 km (Cox et al., 1991a; Gray and Willman, 1991; Lawrence, 1969; VandenBerg, 1978) (Figure 1). Shorter subsidiary folds < 10 km length have wavelengths on the order of 150-500 m (Cox et al., 1991a). The compression also developed a series of west-dipping high-angle reverse faults across the region, with a minor set of east-dipping conjugates (Cox et al., 1991a; Gray and Willman, 1991; Shugg, 2009). Fold-associated fractures formed conduits for gold-bearing fluids during the late stages of regional deformation (Cox et al., 1991b). Mining of the Daylesford Gold Field between 1853-1951 and coincident underground mapping provided valuable insight into the subsurface structures (Maddicks and Butler, 1981). Mining records show west-dipping faults repeat at 60–120

89 m intervals in the Lower Ordovician sandstone-rich rocks near Daylesford (Shugg, 2009). Faults that
90 cross-cut the metasediments contain fault breccia cemented with quartz (Shugg, 2009), and similar
91 quartz-breccia 'reefs' are also found in anticline crests (Cox et al., 1991b). Reefs in the fold hinges
92 and faults can extend for up to 4 km, and were the target for gold miners (Shugg, 2009). The
93 Ordovician turbidites and Devonian granites are overlain by Newer Volcanic basalts, which form a
94 widespread discontinuous plateau and date from 4.5 Ma to ~4.3 ka, with peak activity around 2.6
95 Ma (Gill, 1964; Mcdougall et al., 1966).

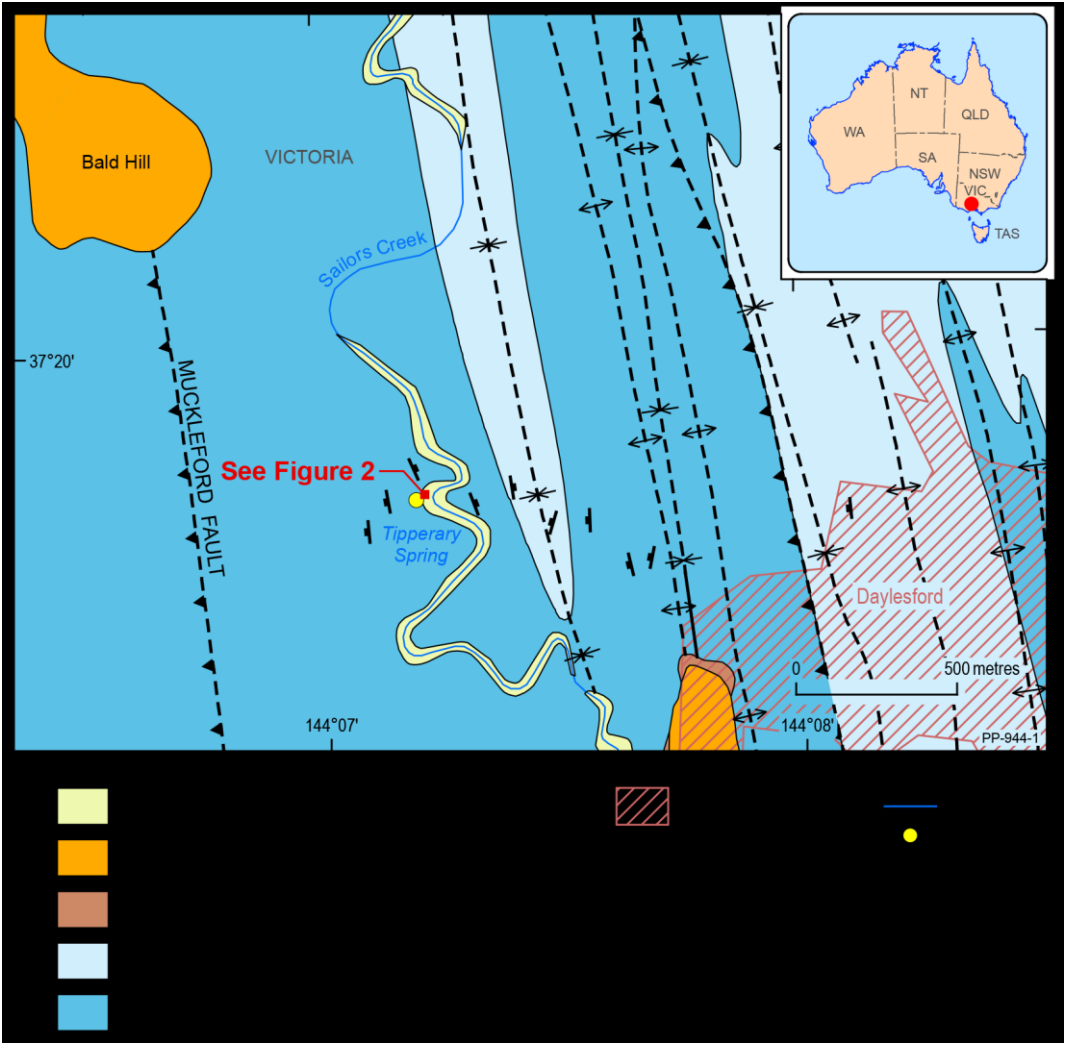
96 The faults, joints, fractures and cleavage developed in the bedrock facilitate groundwater and
97 mineral water circulation (Shugg, 2009). The Ordovician turbidites and Quaternary basalts form
98 regional fractured aquifers. The Ordovician bedrock has two distinct groundwater systems; a
99 shallow fresh groundwater system and a second deeper mineral water system. The two systems mix
100 to varying degrees, especially near the surface expressions of the mineral springs (Shugg, 2004). The
101 CO₂ in the Daylesford Region mineral water is mantle-derived, and so has migrated from a deep-
102 seated source into the Ordovician fractured aquifer (Cartwright et al., 2000; Lawrence, 1969). The
103 mineral waters have a residence time of ~4.5 ka (Cartwright et al., 2002) and are assumed to
104 recharge within the nearby Great Dividing Range, as well as through local volcanics that outcrop at
105 higher elevations in the regional topography (Shugg, 1996).

106 The Daylesford mineral springs are high in calcium, magnesium, and bicarbonates, and so are quite
107 different from typical Australian Na-Cl rich groundwater (Cartwright et al., 2002; Weaver et al.,
108 2006). Individual spring water chemistry has changed little during 20 years of detailed
109 measurements although some springs exhibit mixing with fresh water during discharge (Weaver et
110 al., 2006). The total dissolved CO₂ content of the mineral waters is also consistent across the region
111 (Cartwright et al., 2000; Laing, 1977; Weaver et al., 2006). Spring geochemistry is controlled by fluid-
112 rock interactions facilitated by elevated CO₂ partial pressures (Karolyt  et al., 2017), and, because
113 each spring is geochemically unique (Laing, 1977), it is thought that the subsurface catchment
114 feeding each spring is highly heterogeneous (Weaver et al., 2006).

115 *The study area: Tipperary Spring*

116 The Tipperary Mineral Spring is one of 13 springs around the Daylesford township (Wishart and
117 Wishart, 1990). Tipperary Mineral Springs Reserve is located 2.5 km west of Daylesford
118 (37°20'14.8"S 144°07'14.2"E, Figure 1). The spring eye is located on the west bank of Sailors Creek,
119 beneath a footbridge crossing the creek, demarked by the presence of CO₂ gas bubbles into the

120 creek bed. The bubbles are most apparent during the dry season when water level in the creek drops
121 (Shugg and Brumley, 2003). A hand pump on the east side of Sailors Creek draws water from a
122 borehole which was drilled in 2001. The bore encountered a significant flow of gassy mineral water
123 in a highly fractured horizon at 45 m depth, and the borehole casing was pressure cemented in this
124 portion (Shugg and Brumley, 2003). The mineral water is effervescent. Gases dissolved in the
125 mineral waters of the Daylesford region are reported to range from 88.6 – 95.7 % CO₂ with between
126 0.4 – 0.8 % O₂, 3.9 – 10.2 % N₂ and host trace quantities of He and Ne (Cartwright et al., 2000;
127 Lawrence, 1969). The gasses emitted as bubbles at the seep bed are >99% CO₂ (Karolyte et al., in
128 prep). To date, the characteristics of the degassing, flux and distribution of CO₂ seepage at Tipperary
129 have not been studied in detail.



131 **Figure 1:** Regional geological map, adapted from (Osborne et al., 2002), showing the main geological and structural
132 features of the region north west of Daylesford, Victoria. The location of our study site, Tipperary Spring, is located along
133 Sailors Creek. **Inset:** Map of Australia, showing the location of Daylesford in red.

135 **Methods**

136 Fieldwork at Tipperary was conducted in March 2017, towards the end of the summer when the
137 creek level was low. The fieldwork aimed to collect geological and structural data at the site to
138 observe the style of CO₂ degassing and measure gas fluxes.

139 High precision GPS measurements of bubble locations and outcrop/creek features were taken using
140 an Altus APS3G high precision GNSS survey system for Real Time Kinematic (RTK) position
141 measurements. A base station was set up at each locality and the Rover recorded the UTM
142 coordinates of the feature. The positional accuracy of the RTK equipment is < 1 mm, but human
143 error positioning the RTK will be on the order of < 1 cm. There were some time delays and
144 complications obtaining position measurements due to tree cover and the footbridge which, in
145 addition to the typically sporadic nature of the bubbles streams, meant that the location of the
146 bubble streams was recorded using a local reference grid rather than the RTK. The bubble location
147 error is therefore approximately ~10 cm.

148 CO₂ flux measurements were obtained using a West Systems portable flux system with attached
149 accumulation chamber (type B) and LI-840A CO₂/H₂O gas analyser following the method established
150 by Chiodini et al. (2001). A hollow 50mm PVC pipe frame was attached to the base of the
151 accumulation chamber as a floatation device in order to facilitate flux sampling at the water surface.
152 The base of the accumulation chamber was therefore slightly submerged in water and this change
153 in volume was accounted for when applying the ACK (a conversion factor between ppm/sec
154 (instrument unit) and g/m²/day). ACK temperature and pressure corrections (see Annex A) were
155 made using meteorological measurements recorded at the nearby Ballarat Airport at 10 min
156 intervals (Weatherzone, 2017). Where required, the floating flux chamber was attached to a pole to
157 enable sampling of bubble streams without disturbing the creek sediments.

158 Flux measurements were made at bubbling points. Several readings were also taken at non-bubbling
159 points across the pool to account for background diffuse degassing. The measurement period
160 varied, but generally lasted for 90 seconds or longer, or until the accumulation in the chamber
161 reached a CO₂ concentration of 20,000 ppm (at which point the accuracy of the gas analyser is
162 negatively impacted). Time restraints prevented the quantitative measurement of every mapped
163 bubble point, so our sampling focussed on the most vigorous and continuous bubbling points in the
164 interests of producing the most reliable upper bound estimate of the total CO₂ emission rate. A

165 more detailed discussion of the characteristics and style of the gas emissions at Tipperary is reported
166 in Roberts et al (2018).

167 The presence of 'dry' seeps (CO₂ seepage from rock to atmosphere, not through water) was
168 investigated using a tube connected to a Li-COR 81000A soil gas flux system ('CO₂ sniffer'), allowing
169 CO₂ concentrations of the air to be continuously measured. The inflow tube was used to identify
170 structural features in the outcrop that hosted dry gas seeps.

171 Structural measurements of outcropping bedrock were collected digitally using FieldMove Clino.
172 The area of outcrop and the pool area were calculated from GPS measurements using ArcMap 10.2
173 ©ESRI 2013. Spatial statistical analyses were performed to quantitatively examine seep distributions
174 with respect to geological structures.

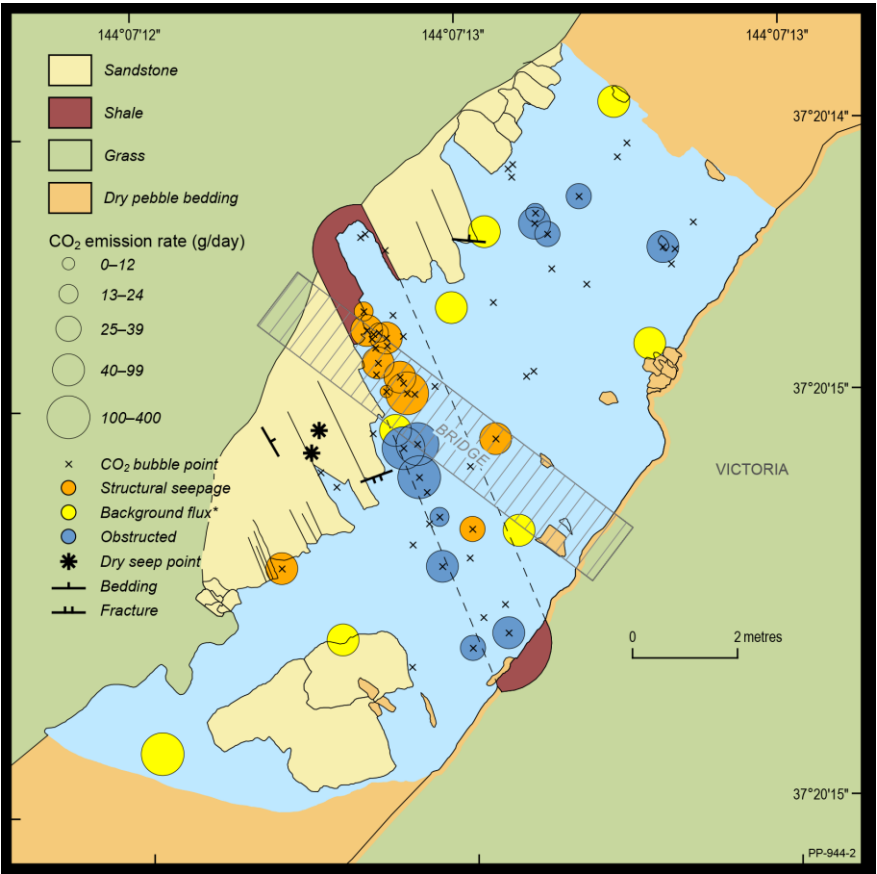
175 **Results**

176 *Field observations*

177 The low creek level in March 2017 meant that a series of isolated pools were found in the bed of
178 Sailors Creek rather than a flowing stream. CO₂ degassing characterised by numerous bubble
179 streams was observed in a single pool of water close to the footbridge near to Tipperary Mineral
180 Spring (Figure 2). The surface area of the pool was ~61.8 m² and water depth was greatest (40 cm)
181 in the centre of the creek.

182 Two units of Ordovician rock crop out in the creek bed. The majority is fine-grained buff coloured
183 massive sandstones that occur in 1 to 3 m thick beds, but a ~2.2 m thick blue-grey shale layer crops
184 out beneath the footbridge. Rock bedding is oriented NW-SE and dips 65 - 80° to the NE (Figure
185 3a,b). In contrast to the sandstone, the shale is thinly bedded (cm scale) with moderately well-
186 developed bedding and parallel foliation. The shale is fissile, and more weathered than the
187 sandstone and is less well exposed at the creek edge. The sandstone is much more cohesive, and
188 while the fracture density is lower than in the shale, the fractures are longer. Three sets of fractures
189 and joints are observed at the outcrop (Figure 3a,c). The primary fracture set trends ~NE-SW and
190 dip steeply to the SE. These vary between ~10 - 50 cm spacing, and fractures in the sandstones
191 extend through the shale. At least two exposed fractures in the sandstone show evidence of vuggy
192 quartz mineralisation. In the shale, the NE-SW fractures are closer spaced (~10 cm) but shorter;
193 often terminating before the sandstone. A second set of shallow-dipping fractures trend ~NW-SE;
194 these are mostly restricted to the sandstone unit, some are mineralised with quartz, several are

195 non-planar or are not laterally pervasive. There is no visible offset along this fracture set, thus they
 196 could classify as joints. A final minor set of near vertical fractures trend E-W. These are poorly
 197 developed, only centimetres in length, with large (~1 m) spacing and no clear evidence of
 198 mineralisation at the outcrop.



199
 200 **Figure 2:** Detailed map of the study area in Sailors Creek at Tipperary Springs Reserve showing the locations of CO₂
 201 bubble streams (cross), and where measured, CO₂ seep rate depicted by the size of the halo (g/d). The colour of the
 202 halo represents whether the bubble visibly emerged from a structural feature (foliation, fracture or bedding plane;
 203 orange), or was not visible either because the seep point was obscured by river sediment or water depth (blue). In
 204 addition, background flux was measured at sites denoted by the yellow dots. Many of the bubble streams are positioned
 205 close to the lower contact between the sandstone and the shale. The principal bedding and fracture orientations are
 206 shown on the map. Two locations of focussed dry seepage were observed, where CO₂ emission was detected from the
 207 outcropping rock (asterisks). The river flows to the North East, but fieldwork was conducted in dry season when creek
 208 fill occurred as isolated pools (though CO₂ bubbling occurred in only one pool).

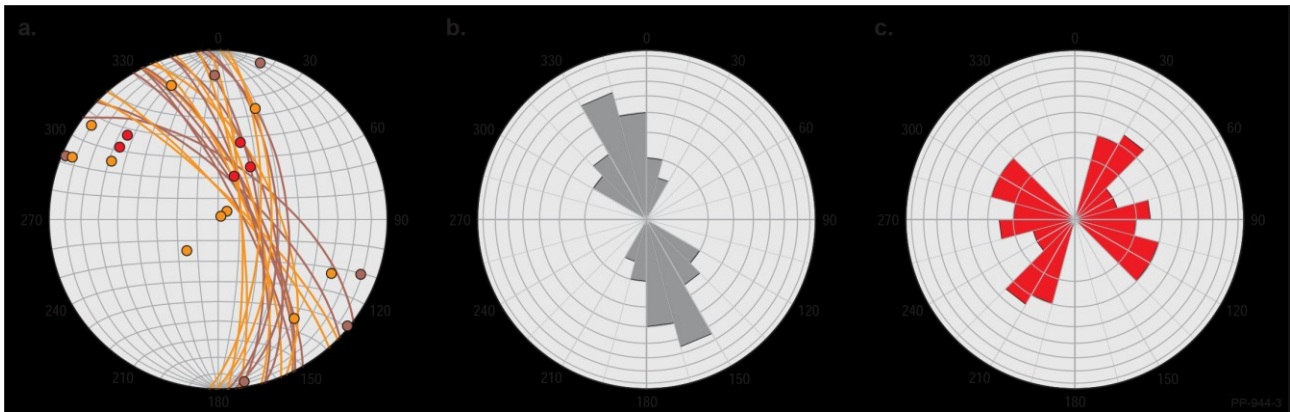


Figure 3: Structural data from outcropping Ordovician turbidites of the Castlemaine Formation in the river bed at Tipperary Spring showing (a) Stereonet of bedding and bedding-parallel cleavage plotted as great circles, and poles to open fracture planes and poles to veins (where sandstones, orange; shales, brown; veins, red); (b) rose diagram of bedding and (c) fracture orientation, including open fractures and veins (shallow dipping fractures will be under-sampled). Structural data was analysed using Orient software (Vollmer, 2015).

CO₂ seepage from submerged rock in Tipperary pool

Figure 2 shows the locations of CO₂ bubble streams in Tipperary pool. The activity of the bubble streams varied in regards to how long they were active (bubbles emitted) and inactive (no bubbles emitted). Some were extremely intermittent, with many minutes, sometimes half an hour before another bubble exhalation, and the bubble streams short lived. Others lasted many seconds, and were comprised of a continuous exhalation of small bubbles. More persistent seeps could bubble for up to seven minutes and were only interrupted with brief pauses. In total, 60 underwater degassing points (bubble streams) were identified and mapped within Tipperary pool, and CO₂ fluxes were measured at 24 (40%) of the locations.

75% of the bubble streams with measured fluxes were located in the shale, and preferentially towards the contact between the shale and the sandstone. CO₂ bubbles emerged along submerged foliation planes within the shale, along bedding planes of the sandstone or at the intersection between the foliation and open fractures or bedding and fractures. 46% (11/24) of the bubble streams with measured fluxes emerged from small fissures offered by dilated foliation or bedding planes, and nearly half of these occurred where open fractures or joints intersect the foliation or bedding plane. The origins of the remaining 13 bubble streams were obscured; either by sediment or because it was not possible to see to the bottom of the pool as the water was quite turbid (due to ferruginous flocculate and algae), a common feature of many of the mineral springs (Shugg and Brumley, 2003).

Background diffuse degassing rate was measured at eight (non-bubbling) locations across Tipperary pool and ranged from 49.4 – 229 g m² d⁻¹ (mean 79.2 g m² d⁻¹). These values were relatively high compared with emissions at other spring-fed pools in the Daylesford region (Roberts et al., in press), and suggests that the dissolved CO₂ content of the pool water is high, but also variable across the pool, but no water samples were collected to verify this. The minimum daily emission rate for the pool was estimated by applying the average of the background readings across the surface area of the pool and neglecting the input of bubbling points giving a value of ~4900 g d⁻¹. Degassing rates at bubbling points ranged from 11.4 to 374 g d⁻¹. These values will represent combined emission of CO₂ from bubbles and water surface degassing. Bubbling rates were greatest at the sandstone-shale contact beneath the footbridge (figure 2). The maximum daily emission rate from the pool was calculated by assuming that bubbling from the point sources was continuous and adding the sum of the maximum measured bubble point emissions (2267 g d⁻¹) to the maximum background degassing rate giving a value of 7170 g d⁻¹. Yearly emissions from the pool can therefore be constrained within the lower and upper estimates of 1.8 – 2.6 t y⁻¹, which correspond to average flux rates across the pool area of 79 - 116 g m² d⁻¹.

CO₂ seepage from outcropping rocks

The CO₂ sniffer detected two locations where atmospheric CO₂ concentrations were up to 6,000 ppm in the dry outcrops on the banks of the creek. In both cases the high CO₂ concentrations were extremely localised, and occurred in jogs or intersections in uncemented, bedding-orthogonal, fractures in sandstones (Figure 4a,c). Further, these concentrations were consistently high. That is, returning to the same location several minutes later, similarly high concentrations from between 2,000 to 6,000 ppm were recorded. Consistently high CO₂ concentrations at these features suggests that seepage was continuous during the survey period (several hours), and also rules out the possibility that elevated CO₂ concentrations were an artefact caused by density-driven pooling of CO₂ degassed from the pool at times of particularly low wind speed. Interestingly, when we poured ~1L water over the seeping fracture the CO₂ concentration returned to background atmospheric levels and took 14 minutes for CO₂ seepage to become re-established. Weak elevations in CO₂ concentration (up to 500 ppm) were detected along a bedding-orthogonal fracture in the foliated shale (Figure 4b,d). However, the area of shale outcrop was less than the sandstone (in part due to bedding thickness, in part due to the morphology of the outcrop) and so we cannot compare instances of CO₂ detection per area of rock.

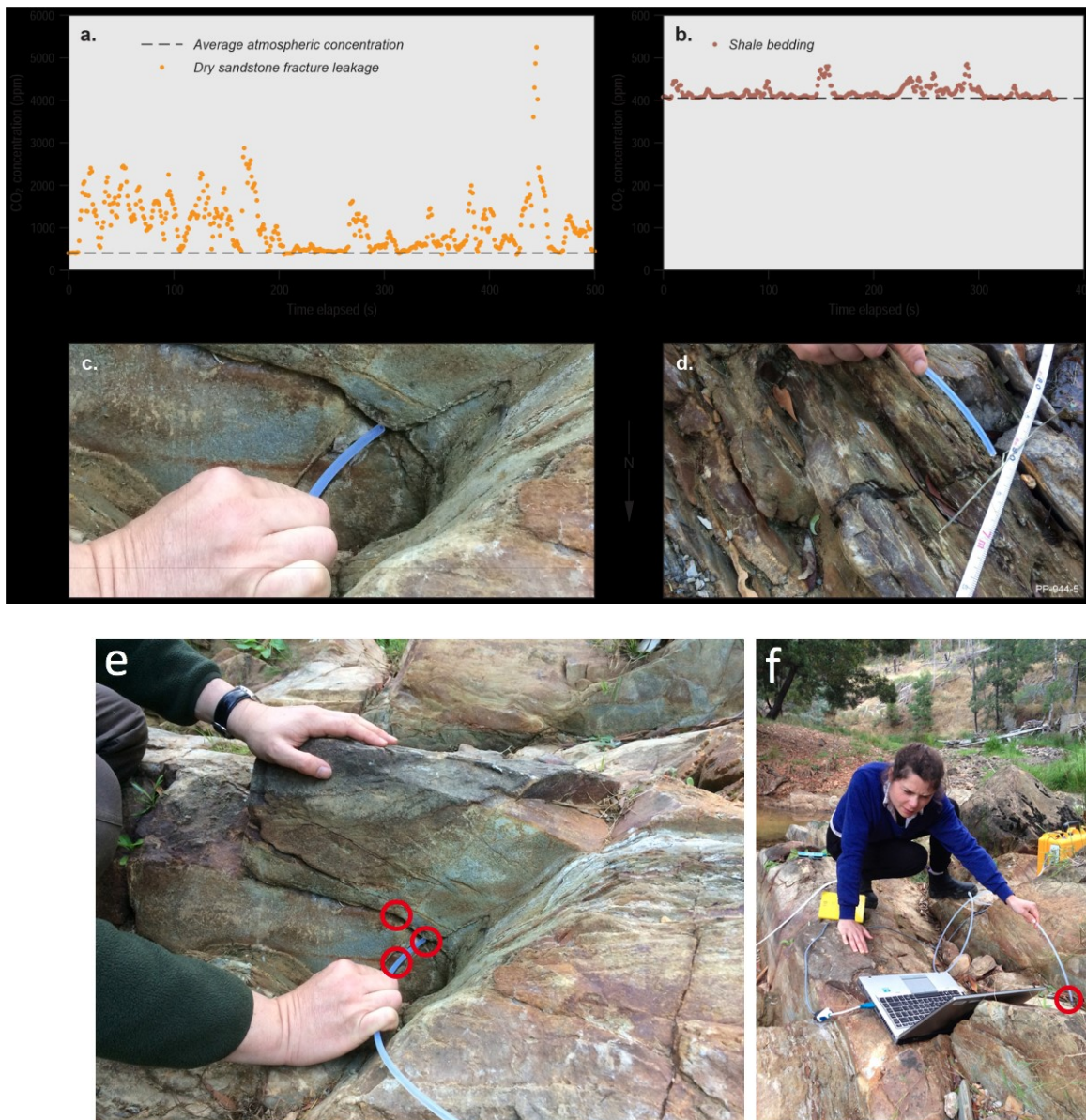


Figure 4: (a) CO₂ concentration data recorded every second by the 'CO₂ sniffer' (a LI-COR 81000A soil gas flux system) when the inflow tube was positioned (a) around a fracture intersection in a sandstone bed (orange) and (b) across shale units (red). Concentration spikes in (a) and (b) indicate where the sniffer passed over points of very localised degassing, and the concentration then varies as the tube is moved along the features, or back and forth over points of high concentration. (c) Photograph of a sandstone bedding surface intersected by two fractures. High CO₂ concentrations shown in (a) were detected at this fracture intersection and at two jogs, detailed in (e). (d) Photograph of a fracture cutting the foliated shale unit. Peaks in CO₂ concentration along this fracture were much lower, as shown in (b). Photographs (e) and (f) show the specific points of CO₂ degassing from the sandstone.

Spatial distribution of seepage

We use a two-point spatial correlation function (TPCF) to quantitatively investigate the alignment of mapped CO₂ bubble streams with geological structures at Tipperary. The TPCF quantifies the departure from homogeneity of a distribution of points, and the distribution of azimuths between

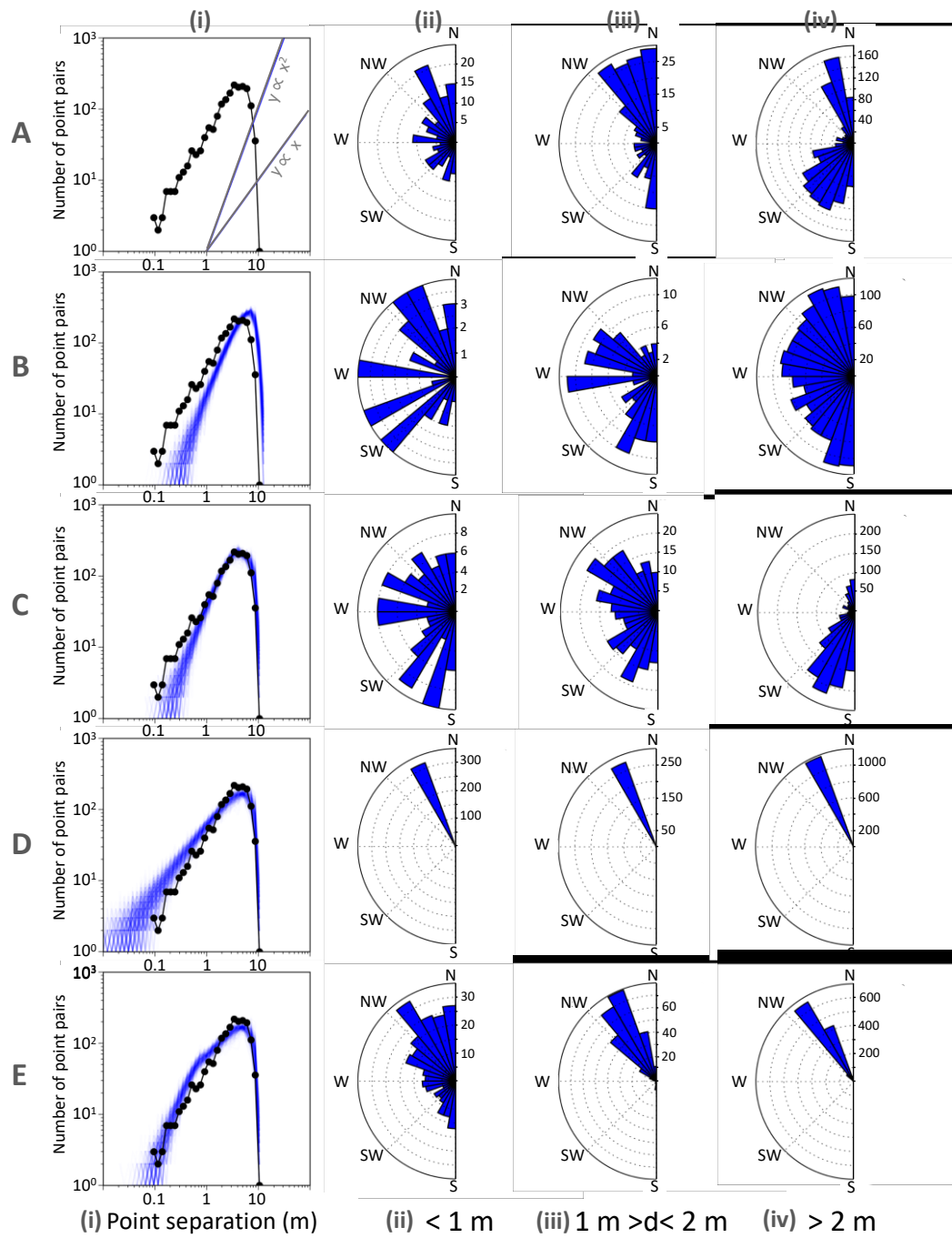
all point pairs can be measured to examine anisotropy in the point distribution. The correlation function is expressed as the probability of finding a pair of points within incremental radius and azimuth. For an ideal scenario with no finite size effects the correlation function will plot as a power law, $P \propto r^\kappa$, where P is probability, r is radius, and the constant κ describes the spatial distribution of points. For randomly distributed points, $\kappa = 2$. If points are clustered, $\kappa < 2$. For points that are distributed on a line, $\kappa = 1$. Other arrangements, such as points distributed on multiple lines, will give κ values between 1 and 2.

The study area is spatially limited; the pond is asymmetric and approximates a 11 x 5 m rectangle. As such, synthetic data was created to act as a 'control' for comparison with the CO₂ bubble stream distributions. The total numbers of measured and synthetic points are the same (60). Synthetic data were generated from multiple random (Poisson) point distributions for different spatial scenarios, including an 11 x 11 m exposure and an 11 x 5 m exposure with long axis orientated NNE, mimicking Tipperary pool which is only 4.4 m at its narrowest point and longer in the NE-SW orientation (see Figure 2). Additional synthetic data were generated for different spatial scenarios, outlined in Table inset Fig 5, including Poisson distribution along a line (orientated 330° within a 10 x 5 m exposure, long axis NNE), or within a given distance of a line, to explore which distribution best describes the observed data.

TPCF results, shown in Figure 5, are presented for the bubble points and for synthetic scenarios. The roll-off at distances > 4 m is a finite size (censoring) effect caused by the spatial extent of the outcrop (e.g. Bonnet et al., 2001). For the synthetic data, κ is affected by the dimensions of the study area (outcrop/pool); for scenario B, random points in a 10 m square, κ is close to 2 (random) whereas for scenario C, κ is ~ 1.75 . Since κ values < 2 indicate clustering of point data, even for Poisson data, this is a finite-size (censoring) effect caused by the spatial extent of the outcrop creating an artificial alignment amongst point data. Reducing the width of the rectangle reduces the κ value, until the extreme case, scenario D, where points are distributed on a line, when $\kappa = 1$. For bubble data, $\kappa = \sim 1.5$. This TPCF pattern is best modelled by scenario E, where the width of rectangle is thinner than the shale outcrop.

Correlation function

Point pair azimuths



306

Point data		Description
A		CO ₂ bubble locations at Tipperary spring
Synthetic data	B	Points randomly distributed within 11 x 11 m square.
	C	Points randomly distributed within 11 x 5 m rectangle, long axis orientated NNE (simulating the outcrop extent).
	D	Points randomly distributed along a line, 11 m long, orientated ~NW (simulating points located directly along a fault or geological contact).

	E	Points randomly distributed within 11 x 1 m rectangle, long axis orientated ~NW (simulating points located within a bed, or around a fault or geological contact)
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307 **Figure 5:** (i) Point-distance correlation functions for observed seep pairs (black) and synthetic point simulations (blue)
308 for scenarios A to E. Polar plots show the azimuths and number of point pairs with separation distances (ii) below 1 m;
309 (iii) greater than or equal to 1m but less than 2 m; and (iv) greater than or equal to 2 m but less than 10 m. Roll-off in
310 the TPCF occurs at ~4 m separation distance due to the outcrop extent. **Table inset:** Summary of the different spatial
311 scenarios for seep point data and synthetic data.

312 Point pair azimuths at different point separation distances are shown in Figure 5 for bubble point
313 (scenario A) and synthetic (scenarios B-E) data. More point pairs are located at shorter distances in
314 the bubble data than in the synthetic data; there are over twice as many bubble point pairs within
315 less than 1 m of each other than for the synthetic data C (164:75). Since the total number of points
316 in the datasets are the same, these differences illustrate that the bubble points are more clustered
317 than in all synthetic datasets.

318 At point separation distances above 2 m the finite size effect caused by the orientation of the study
319 area clearly influences the point pair azimuths. In scenario C the rectangle is orientated NNE like the
320 Tipperary pool, whereas other synthetic scenarios are orientated NW, like the bedding at Tipperary.
321 The >2 m point pair azimuths in these synthetic scenarios clearly reflect the orientation of the
322 rectangle long axis (Fig 5iv). The effect of the orientation of Tipperary pool is evident in the bubble
323 point pair azimuths, as is the control of the NNW trending bedding/foliation 5A(iv). The control of
324 bedding/foliation on bubble pair azimuths continues to be visible at point pair distances below 2 m
325 5A(ii,iii); 38% (63 pairs) of bubbles located within <1 m of each other, and 51% of bubbles located
326 between 1 – 2 m of each other exhibit a NNW-SSE (315°–360°) orientation. In contrast, since
327 synthetic data are all randomly distributed in a given space, the dimensions of the study area are
328 not visible in the point pair azimuths at distances <2 m (except for scenario D, where point pair
329 azimuths are the same at all separation distances).

330 While bubbling points were observed in the field to be located along bedding, foliation and fracture
331 planes, the point azimuths < 2 m do not exhibit very clear spatial trends other than the bedding and
332 foliation. At Tipperary, a range of fracture orientations were measured (see Fig 3c) with dominant
333 sets trending NE-SE and NW-SE. Bubble pairs do show peaks in these orientations at < 2 m
334 separation, but it is difficult to distinguish these from noise.

335 Discussion

336 *The role of geological structures and CO₂ seepage at Tipperary*

337 Central Victorian mineral water springs are commonly channelled by regional thrust faults and can
338 emerge close to anticline crests (Shugg, 2009). Although obscured in the field area, the regional
339 geological map shows an inferred NNW-SSE trending anticline to the West of Sailors Creek, its
340 projected axis passing less than 20 meters from the creek. An inferred NW-SE fault runs in the same
341 orientation as the creek but is mapped as terminating before intersecting the creek (Figure 1). In
342 1912 the Daylesford Borough Engineer developed a cement-lined pit approximately 50 m SW of the
343 current location of CO₂ degassing. This pit is now in disrepair, but was built to channel the spring
344 waters, for ease of access to the mineral spring. The engineer's sketches of the area around the pit
345 record a NE-SW trending fault and a NNW-SSE trending fold, and Shugg (2004) interprets that
346 Tipperary Mineral Spring is located on the surface intersection of a thrust fault. Today, there is no
347 clear evidence of this fault at outcrop. A borehole drilled in 2001 (for the handpump) is likely to have
348 intersected this fault as indicated by the flow of gassy mineral water encountered at 45 m depth
349 (Shugg, 2004). The flow of mineral waters carrying dissolved CO₂ from depth towards the surface
350 may be guided by the geological structures such as the fault and/or the nearby anticline, similar to
351 the hypothesis of Shugg (2009). The presence of ponded water in an otherwise dry creek during the
352 dry season implies that mineral waters are seeping into the creek bed at the location of degassing.
353 However, the mineral waters probably degas CO₂ during their ascent to surface; we observed dry
354 seepage from outcropping rocks, while at nearby springs down-hole camera surveys found bubbles
355 starting to form around 20–30 m below the water table (Shugg 2009). When two-phase flow
356 establishes, the CO₂ may migrate to surface via different pathways to its 'parent' water, depending
357 on the hydraulic properties of the available flow pathways and water table depth. There is no
358 appreciable thermal anomaly between the mineral waters and the surrounding groundwater
359 (Weaver et al., 2006), so they are not ascending due to thermal buoyancy drive. Instead they may
360 be migrating towards the surface due to a combination of hydraulic head and the fluid flow
361 pathways offered by nearby structures, enhanced by buoyancy from gas lift due to CO₂ ebullition as
362 the waters depressurise during ascent.

363 CO₂ seepage at Tipperary spring concentrates near the western sandstone-shale contact. Some 81%
364 of total measured bubble stream emissions emerge from the shale dominated features in the river
365 bed and we detected extremely localised dry seepage from open fractures within outcropping
366 sandstone and shale. The bedding and foliation orientation of rocks exposed in Sailors Creek follows
367 the regional trend from NNW-SSE Devonian compression. Our spatial statistical analyses find that

368 bubble point data exhibit this NNW-SSE (150-170°) trend at all point separation distances. Bubble
369 points located within <2 m of each other show other preferred alignments (NE-SW and SE-NW, NNE-
370 SSW, ENE-WSW) but these trends are weak compared to the NNW orientations. Seepage mostly
371 occurred in a narrow region, ~1 m width. In the field, we noted that bubble locations appeared to
372 be primarily controlled by bedding and foliation planes, but also by fractures and joints across both
373 the sandstone and shale members. Thus, while regional structures may govern mineral water and
374 CO₂ flow (Shugg, 2009), it seems that primary features (the sandstone-shale contact) may control
375 fluid flow in the deep and shallow subsurface, and at very shallow depths the small secondary
376 structures (fractures, foliation) offer pathways to surface.

377 What is unusual at Tipperary is that gas primarily discharges from shales. Mudrocks and shales
378 typically have low permeabilities, and high capillary entry pressures for two-phase flow, which
379 makes them good seals for conventional hydrocarbon traps. At other sites around Daylesford, such
380 as Sutton Spring, mineral water and gas discharges from the joints and fracture faces in sandstone
381 beds (Shugg, 2009). These sandstones form the regional aquifer. Within these sandstone units
382 intergranular porosity is limited to certain horizons. Therefore, groundwater flow is predominantly
383 hosted by fractures and joints. Observations from exposed bedrock at Tipperary suggest that bulk
384 rock permeability is most likely offered by the primary fracture set (NE-SW trend) together with the
385 bedding. However, at Tipperary, our observations, corroborated by spatial statistical analyses, find
386 that CO₂ bubbles preferentially emerge from foliation and fracture intersections in the shale. This
387 indicates that in the shallow subsurface the high density of subvertical foliation and bedding-
388 orthogonal fractures in the shale must be more transmissive than bedding and fracture planes in
389 the sandstone. At outcrop, the fractured, folded and uplifted shales of the Ordovician succession
390 clearly are not sealing. This could be due to unloading and weathering, and so these pathways have
391 opened only close to the surface. Conversely, the bulk permeability of the shale units may be greater
392 than the sandstone for these units. Figure 6 schematically summarises the proposed mechanism for
393 CO₂ delivery to the creek bed at Tipperary.

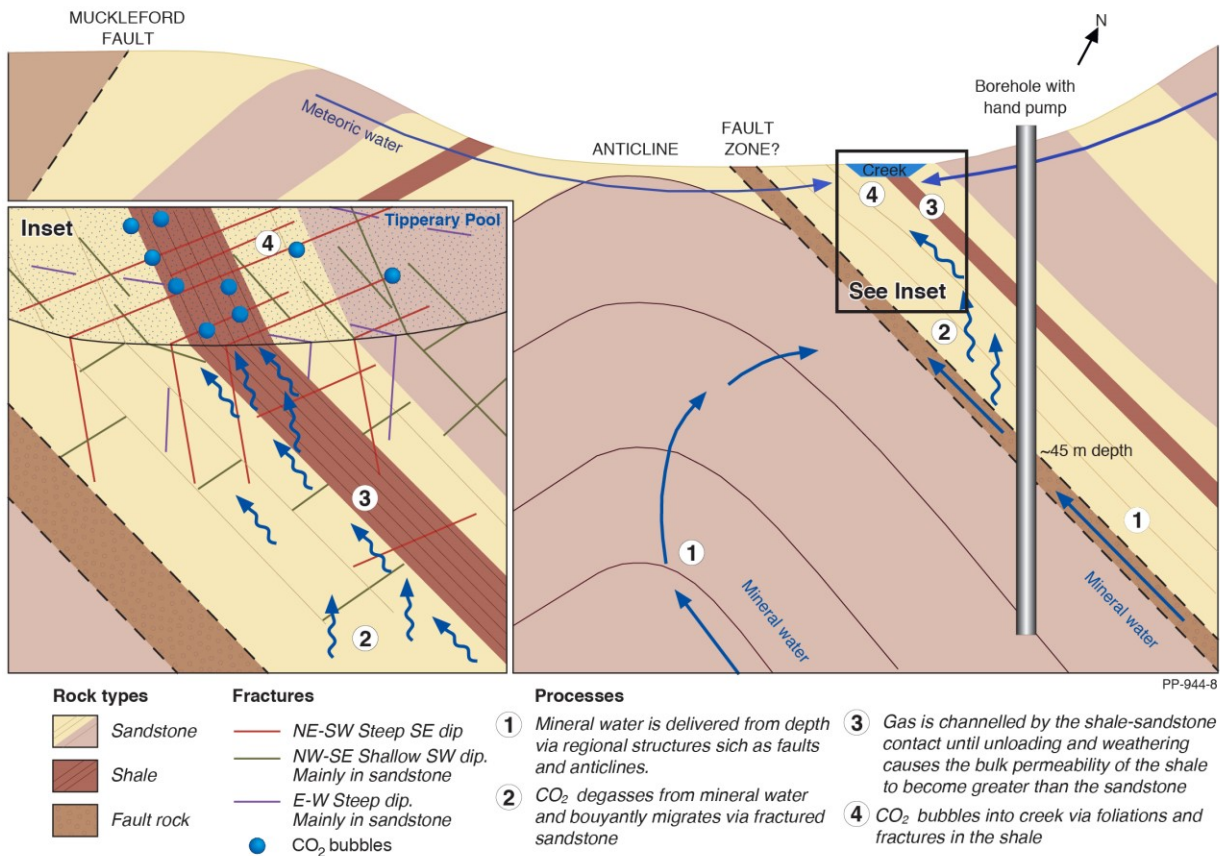


Figure 6: Schematic 2D cross section (not to scale) of proposed model for CO₂ and mineral water flow pathways that give rise to Tipperary Mineral Spring and CO₂ seep. Inset: schematic 2.5D closeup of Tipperary Pool. While the shale may not be transmissive to fluids at depths where foliation and fractures are closed by overburden pressure, we propose that in the shallow subsurface unloading and weathering opens bedding, foliation and fractures enabling the shale to transmit fluids more readily than the fractured sandstone aquifer rocks. This causes the majority of CO₂ to be emitted via well-connected flow pathways in the shale unit in Tipperary Pool, and manifests as numerous and intermittent low flux bubble streams. CO₂ that is emitted straight to atmosphere ('dry seepage') is not intermittent. This implies that the turning 'on' and 'off' of bubble streams may result from capillary flow processes in the very shallow subsurface.

Other seeps worldwide emerge from clays. For example, in the Cheb Basin, CO₂ degassing close to a fault zone in clay dominated rocks occurs as highly localised emissions from fine fractures, facilitated by "micro-channels" in the clays which originated from shear (Bankwitz et al., 2003). Where low permeability rocks outcrop in Italy, CO₂ degassing occurs as vent like emissions rather than as springs or spring associated emissions, which more commonly occur from high permeability rocks (Roberts et al., 2014). However, at Tipperary, what is surprising is that CO₂ preferentially emerges from the shales rather than the sandstones.

That said, CO₂ seepage is not confined to the shale. Seepage occurs from sandstones submerged in Tipperary pool, and the CO₂ sniffer detected high CO₂ emissions from isolated points in the

412 outcropping sandstone. Therefore there are gas flow pathways in the sandstone, but there are
413 fewer pathways in the sandstone than in the shales (where gas emission is greater), and these
414 pathways are extremely localised; occurring at jogs and intersections along low-dip bedding-
415 orthogonal fractures, where they intersected the bedding plane (Figure 5e).

416 Interestingly, the sniffer results indicate that it is likely that dry CO₂ seepage is greater from the
417 outcropping sandstone than from outcropping shale. This is in contrast to CO₂ fluxes measured in
418 Tipperary pool where more numerous and distributed bubble streams occur in the shale, and 75%
419 of the total CO₂ flux via bubbles from Tipperary Pool is occurring from the shales. It is possible that
420 this is a sampling artefact; the seep area is limited, the shale bed is thinner than the sandstones,
421 and the area of outcrop is much smaller for the shale because it has preferentially eroded on the
422 creek banks. If this is a real signal, there could be several explanations for the contrasting behaviour
423 of the seeps through water and into air. Firstly, the rate of CO₂ seepage through the two lithologies
424 could be the same but is occurring via distributed pathways (lots of small fractures and bedding
425 partings) in the shale, with fewer localised high flux fracture-bedding intersections in the sandstone.
426 As the shale was more foliated and thinly bedded, there were many more bedding parallel features
427 to permit flow and so facilitate distributed seepage than in the massive bedded sandstone.
428 Secondly, the outcrop style varies between the two lithologies: the sandstone stands proud of the
429 surface and some individual bedding planes are exposed, whereas the shale is more eroded and the
430 bedding is only viewed end-on. This means that the fractures that are low-dip (which are the ones
431 that host the high dry seepage from the sandstone) are exposed in the sandstone, but are unlikely
432 to be exposed in the shale at this site. Thirdly, flow pathways in the sandstone might be more likely
433 to become obstructed by river sediments than the smaller aperture features in the shale. Regardless
434 of the reason, our observations suggest that flow pathways in the very shallowest subsurface, and
435 therefore how CO₂ seeps present, are highly sensitive to local conditions.

436 *CO₂ flux at Tipperary*

437 Estimating total CO₂ flux at Tipperary Spring is challenging given the intermittency of the CO₂ bubble
438 streams. Bubbling, and therefore CO₂ flux, was not continuous in the pool. The flux of CO₂ from
439 depth is probably continuous, but the bubbles are intermittent either due to high connectivity of
440 the flow pathways (with flow paths turning 'on' and 'off') and/or due to water saturation of the flow
441 pathways; CO₂ gas pressure must build enough to overcome capillary flow pressure, and the
442 pressure of the water in the fracture. Such temporal and spatial variability has been observed at

443 other CO₂ seeps including Laacher See (Germany - CO₂ bubbling is observed from the floor of a crater
444 lake), Panarea (Italy - submarine geothermal region) and at the QICS project (Scotland - simulated
445 CO₂ leak to the marine environment) Blackford et al. (2015) and Carammana pers. comm (2017). At
446 a larger spatial scale, temporal and spatial variability in CO₂ emission has been observed at the Little
447 Grand and Salt Wash faults in Utah over tens of thousands of years (Burnside et al., 2013). As such,
448 intermittency of gas bubbling could be a universal phenomenon associated with gas flux into
449 heterogeneous water-saturated media. This phenomenon is not restricted to CO₂. For example, the
450 authors have observed intermittent bubbling of gases (predominantly nitrogen, but including CO₂,
451 CH₄ and other short chain hydrocarbons) into creek beds in Northumberland (UK), and presumed to
452 source from abandoned underground coal mines, which are common in this region.

453 Dynamic seepage has implications for strategies for sampling of natural gases, and also for
454 estimating gas fluxes or total emissions. At Tipperary, the minimum total flux can be estimated from
455 background diffuse degassing ($79.2 \text{ g m}^{-2}\text{d}^{-1}$ or 4 kg y^{-1}), which does not include the contribution of
456 individual bubbling seeps. Maximum flux can be estimated by assuming all measured bubble
457 streams are active simultaneously, which equates to $116 \text{ g m}^{-2}\text{d}^{-1}$. However, since few bubble
458 streams were active at the same time, this is an overestimate. In addition, our estimates do not
459 consider dry CO₂ seepage from rocks by the pool, CO₂ dissolution (if the pool is not already
460 saturated), or seasonal changes in the CO₂ emission.

461 Previous studies at natural CO₂ seeps find a range of CO₂ fluxes over several orders of magnitude,
462 which poses challenges for the selection of appropriate monitoring devices and approaches. The
463 rate of degassing depends on factors including soil and rock permeability, hydrogeological regime,
464 and nature of the CO₂ source (Annunziatellis et al., 2008, Kirk et al., 2011). Fluxes at dry seeps such
465 as mofettes can be very high e.g. $9000 \text{ g m}^{-2}\text{d}^{-1}$ at Florina (Greece) and $125,000 \text{ g m}^{-2} \text{ d}^{-1}$ in the Cheb
466 Basin (Germany/Czech Republic) (Nickschick et al., 2015). But mofette systems are different from
467 CO₂ degassing at mineral springs. Recent work at travertine bearing fault systems report fluxes that
468 are more similar to Tipperary; maximum CO₂ fluxes were $191 \text{ g m}^{-2}\text{d}^{-1}$ at the Bongwana Fault (South
469 Africa) (Bond et al., 2017) and calculated from travertine mass balance to be $1,472 \pm 677$ and 18.8
470 $\pm 8.7 \text{ g m}^{-2}\text{d}^{-1}$ at two sites in Utah (USA) (Burnside et al., 2013).

471 Natural non-volcanic seeps are the most appropriate analogues for seeps that might potentially
472 develop above engineered carbon stores, if injected CO₂ seeps to the surface by natural CO₂
473 pathways. However there are limitations to their comparability. Storage sites will be selected for

specific sealing characteristics. In contrast, surface seepage at natural CO₂ seeps occur *because* the geology is not ideal for long term CO₂ trapping; the geology around Daylesford is composed of highly heterogeneous and tectonised sediments crossed by faults. Faulted reservoirs with heterogeneous or poorly permeable overburdens will probably not be selected for long term geological storage. In addition, natural CO₂ seeps will be migrating by natural fluid pathways whereas the greatest risks of CO₂ leakage from engineered CO₂ stores are man-made pathways, such as improperly sealed boreholes (IPCC, 2005) or geomechanical effects from the pressure response to CO₂ injection (Verdon et al., 2013). That said, natural CO₂ seeps may still be comparable to leakage through the overburden, independent of the leakage pathways from the reservoir, and seepage through clay formations, can serve analogues of CO₂ migration through cap rocks.

Implications for CCS

It is important to assure regulatory bodies and the public of CO₂ storage integrity. This includes demonstrating capability to (i) select storage sites that will successfully retain CO₂ in the subsurface, and (ii) identify potential CO₂ leakage and (iii) quantify any leaked CO₂.

In the case of CO₂ migration from onshore engineered storage sites, if the leaked CO₂ migrates to the near surface it could dissolve into groundwaters (and perhaps emerge as a dissolved constituent of groundwaters at natural springs), seep to atmosphere as a dry gas, or seep into water bodies such as lakes or rivers. Where migrating CO₂ dissolves into groundwaters, the groundwater flow systems will then govern its flow path, and only at shallow depth will decreasing pressures cause gas ebullition and facilitate the ascent of a separate gas phase. Indeed, studies of onshore natural analogues and field sites find that CO₂ seeps are more likely to emerge in topographic low points where there may be rivers or lakes, though there are examples of seeps that buck this trend (e.g. if flow is fault controlled) (Roberts et al., 2014).

In this work, we examine the surface expression of CO₂ seepage originating from transport of CO₂-rich regional groundwaters. We find that, while regional features may govern CO₂ delivery, in the shallow subsurface CO₂ pathways are localised to small scale geological features, and that fluxes are intermittent and consequently difficult to quantify due to the intermittency of bubbling pathways.

To date, most research has focussed on predicting the large-scale geological features that may enable CO₂ to migrate from the storage reservoir such as large faults, boreholes or gas chimneys (IEAGHG, 2017). Such macroscale (seismically resolvable) features are likely to be known about at the site characterisation phase of a project. However, shallow crustal processes change the rock

properties that affect CO₂ spread and delivery to surface. Different, smaller scale geological features, that are not likely to be seismically resolvable, may become important controls on CO₂ flow in the shallow subsurface. At Tipperary, CO₂ seep distribution is controlled by microscale features such as foliation and bedding planes, joints and fractures in outcropping rock, probably dilated by uplift and weathering, which leads to degassing from a shale formation that is typically sealing. These observations support previous research investigating the role of topography and lithology in CO₂ seep location and characteristics (Roberts et al., 2014), and has important consequences for the design of CCS monitoring approaches. Surface monitoring programmes must focus on more than the processes and pathways governing leakage at depth; they must also consider how the CO₂ fluids leaked by natural or man-made pathways might disperse in the near surface and be expressed at the surface. These shallow processes will inform the design of the right monitoring tools and monitoring locations.

Our work thus provides insight into the scale of which geological features control CO₂ flow and the spatial and temporal variability of CO₂ leakage. Essentially, site characterisation during site selection and monitoring design must assess the geology and hydrogeology at a range of spatial scales. Surface processes, often overlooked, will govern the style and location of leakage, and so should inform the design of appropriate monitoring strategies.

Conclusions

We have studied the location and characteristics of CO₂ emission at Tipperary natural CO₂ seep in Daylesford, Victoria (Australia) as an analogue for leakage from engineered CO₂ stores. Seepage largely occurs as bubble streams in a pool in Sailors Creek, close to the Tipperary mineral springs which have high dissolved CO₂-content. We also observed CO₂ degassing from subaerial rock outcrop. Observation and spatial statistical analyses find that at a meso-scale (multiple meters) the location of CO₂ bubble streams are controlled by the sandstone-shale geological contact. At a smaller (meter to centimetre) scale, gas emission is controlled by structural features, primarily fractures intersecting the foliation or bedding planes. The intermittency of the bubble streams, and their distribution, makes CO₂ flux challenging to quantify. Unusually, CO₂ emission is greatest from the shale, rather than the sandstone that forms the regional aquifer. Surface processes are likely to be affecting rock transmissivity, which governs CO₂ flow at the near surface. Our work has important implications for characterising and monitoring of CO₂ stores: microscale features and near surface processes can have significant effect on CO₂ leak locations and rates. Flow pathways through the

536 very shallowest part of the subsurface are highly dependent on local conditions, and may produce
537 the highest flux in counter-intuitive locations (e.g. hosted by the 'low permeability' shales at
538 Tipperary). Understanding of shallow crustal processes and specific site conditions are essential to
539 inform the design of effective surface monitoring tools and approaches. Secondly, should leakage
540 from the storage reservoir occur, the surface leak identification and quantitation approaches must
541 be extended to consider intermittent or variable CO₂ emission rates.

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558 **Annex A: Accumulator chamber factor for CO₂ flux measurements**

559 To convert the rate of change in CO₂ concentration measured in the accumulation change (e.g. in
560 ppm/s) to a flux (mole/m²/day), the rate needs to be multiplied by a correction factor which
561 considers the volume of the chamber, temperature and pressure:

$$562 \quad K = \frac{86400 \cdot P}{10^6 \cdot R \cdot T_k} \cdot \frac{V}{A}$$

563 where

- 564 • P is the barometric pressure expressed in mBar

- 565 • R is the gas constant 0.0831451 bar L K⁻¹ mol⁻¹
- 566 • T_k is the air temperature expressed in degrees Kelvin
- 567 • V is the chamber net volume in cubic meters (less the portion of the chamber submerged to
- 568 create a seal on the water surface)
- 569 • A is the chamber inlet area in square meters

570

571 **Data Availability Statement**

572 All data (precise bubble locations and distributions, fluxes, and whether bubbling occurred at a
 573 fracture or foliation/bedding at Tipperary pool), are available from the UKCCSRC Data and
 574 Information Archive, under the DOI: (to be added).

575

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